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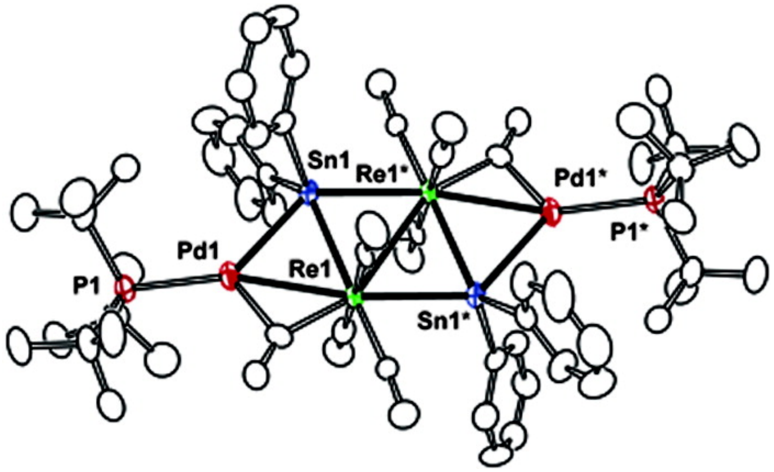

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New Rhenium−Tin Cluster Adds Palladium Phosphine Groups across Re−Sn Bonds

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Tin is widely used as a modifier for transition metal catalysts to improve their reactivities and product selectivities.[1,2] We have recently shown that Ph_3SnH is a good reagent for the introduction of large numbers of phenyl-substituted tin ligands into carbidopentaruthenium carbonyl complexes.[3] Surprisingly, there are very few examples of polynuclear rhenium carbonyl cluster complexes containing tin ligands.[4] We have now found that Ph_3SnH also reacts with the reactive rhenium complex $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}C(H)C(H)Bu]$[5] to yield the new dirhenium−ditin complex $Re_2(CO)_8(\mu\text{-}SnPh_2)_2$, **1**, in 52% yield when allowed to react in hexane solvent at reflux for 2 h.[6] Compound **1** was characterized by single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1.[7] The crystal of **1** contains two crystallographically centrosymmetric molecules in the asymmetric unit. The molecule contains two $Re(CO)_4$ groups that are linked by two bridging $SnPh_2$ groups, see Scheme 1.

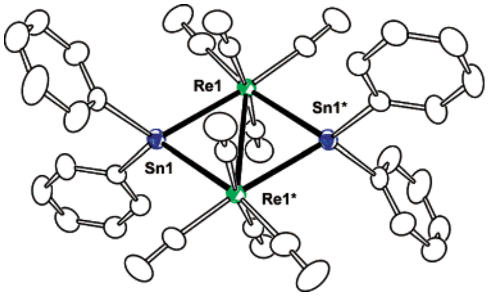
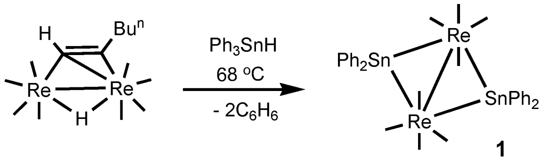


Figure 1. ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}SnPh_2)_2$, **1**, showing 40% thermal ellipsoid probability. Selected bond distances (Å): molecule 1: Re(1)−Re(1*) = 3.1971(4), Re(1)−Sn(1) = 2.7429(4), Re(1)−Sn(1*) = 2.7675(4); molecule 2: Re(2)−Re(2*) = 3.1902(4) Å, Re(2)−Sn(2) = 2.7445(4) Å, Re(2)−Sn(2*) = 2.7682(5) Å.

Scheme 1



Benzene, a coproduct, accounts for the fate of the cleaved phenyl groups. According to electron counting procedures, the complex should contain a Re−Re bond for each metal atom to achieve the 18-electron configuration. The Re−Re bond distance at 3.1971(4) Å [3.1902(4) Å] is long, but short enough to allow for some direct Re−Re interaction. The Re−Re distance in $Re_2(CO)_{10}$, which contains a Re−Re single bond, is 3.042(1) Å.[8] To understand the metal−metal bonding in **1** better, we have performed Fenske−Hall molecular orbital calculations.[9] The results of these calculations show that the metal−metal bonding in **1** is strongly dominated by Re−Sn interactions. This is illustrated by the contour diagram for the b_{1g} HOMO, shown in Figure 2A, which is representative of these interactions and is supported by the structural analysis which shows normal Re−Sn distances, Re−Sn = 2.7429(4) Å [2.7445(4) Å] and 2.7675(4) [2.7682(5) Å]. The only significant direct Re−Re bonding interaction is shown in the a_g HOMO-2, shown in Figure 2B.

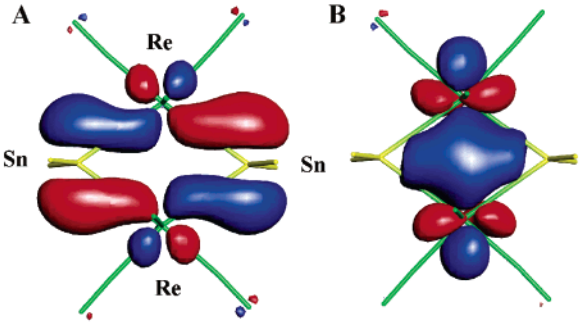


Figure 2. (A) HOMO, b_{1g} orbital of **1**. (B) HOMO-2, a_g orbital of **1**.

The importance of the Re−Sn interactions in **1** is further demonstrated by its reaction with $Pd(PBu^t_3)_2$. The reaction of **1** with $Pd(PBu^t_3)_2$ at room temperature provided the novel complex $Pd_2Re_2(CO)_8(\mu\text{-}SnPh_2)_2(PBu^t_3)_2$, **2**, in 67% yield.[10] The structure of **2** was also established crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 3.[11] Complex **2** is crystallographically centrosymmetric. The molecule can be viewed as a bis-$Pd(PBu^t_3)$ adduct of **1**; that is, two $Pd(PBu^t_3)$ groups were added to the intact molecule **1**. These groups occupy bridging positions across two of the four Re−Sn bonds in **1**, see Scheme 2.

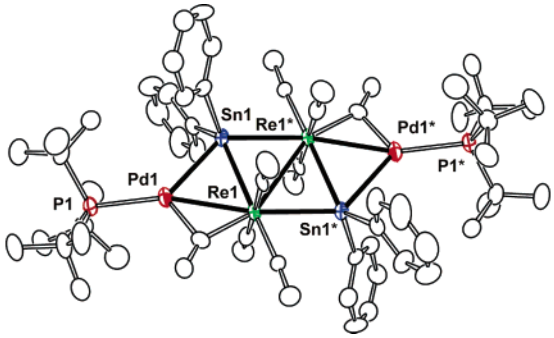


Figure 3. ORTEP diagram of the molecular structure of $Pd_2Re_2(CO)_8(\mu\text{-}SnPh_2)_2(PBu^t)_2$, **2**, showing 30% thermal ellipsoid probability. Selected bond distances (Å): Re−Re = 3.262(1), Re(1)−Sn(1) = 2.7674(5), Re(1)−Sn(1*) = 2.8215(5), Re(1)−Pd(1) = 2.8580(5), Pd(1)−Sn(1) = 2.7185(7), Pd(1)−P(1) = 2.4093(17).

Each Re−Pd bond contains a semi-bridging carbonyl ligand. The Re−Pd bond distance is normal, 2.8580(5) Å. The Pd−Sn bond distance, 2.7185(7) Å, is significantly longer than that typically found for Pd−Sn single bonds, e.g. 2.6082(3) Å observed in Pd-

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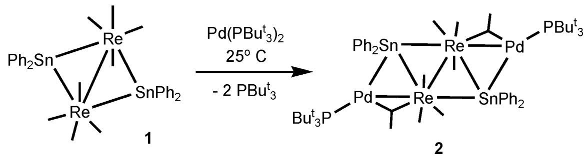
Scheme 2



(PBu$^t_2$CH$_2$CH$_2$PBu$^t_2$)(H)SnMe$_3$.[12] The Re−Re bond in **2** is even longer than that in **1**, Re(1)−Re(1) = 3.262(1) Å. The palladium-bridged Re−Sn bond, Re(1)−Sn(1) = 2.7674(5) Å, is not significantly different from that in **1**, but curiously, the Re−Sn bond that is not directly bonded to the palladium atoms is significantly elongated, Re(1)−Sn(1*) = 2.8215(5) Å.

To understand the nature of the bonding, we have performed Fenske−Hall molecular orbital calculations on **2** by adding two Pd(PH$_3$) groups to the model developed for **1** above[9] using idealized C_{2h} symmetry. Contour diagrams for the HOMO, 2a$_g$ and HOMO-1, 1a$_g$ for **2** derived from the HOMO and HOMO-2 of **1** are shown in Figure 4, A and B, respectively. As can be seen, the Re−Sn overlap increases for the Pd-bridged Re−Sn bond and decreases for the unbridged Re−Sn bond in the HOMO. This explains the weakening and lengthening of the unbridged Re−Sn bond. The Re−Pd and Pd−Sn interactions are shown by the HOMO-1 in Figure 4B. As can be seen, this bond is dominated by Re−Pd interactions. The Pd−Sn interactions are minimal, which explains why the Pd−Sn bond distance is so long.

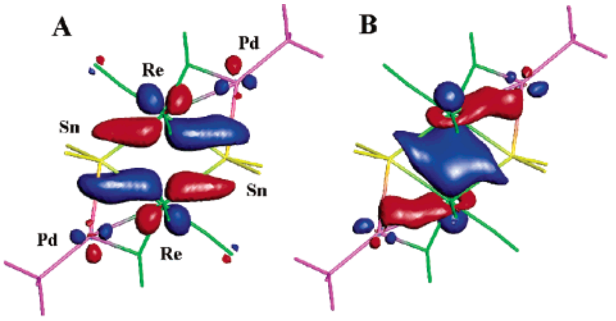


Figure 4. (A) HOMO, 2a$_g$ orbital of **2**. (B) HOMO-1, 1a$_g$ orbital of **2**.

We have recently demonstrated the ability of Pd(PBu$^t_3$) and Pt(PBu$^t_3$) groups to form electron-deficient bonds across transition metal−transition metal bonds in polynuclear metal carbonyl complexes.[13] These new results now show that Pd(PBu$^t_3$) groups can also form electron-deficient metal−metal bonds across transition metal−main group metal bonds. Further studies are in progress. The facile introduction of tin- and palladium-containing groups into metal carbonyl clusters may make available a range of new trimetallic carbonyl cluster complexes that can serve as precursors to new nanoclusters containing tin that could find applications in heterogeneous catalysis.[2,14]

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Supporting Information Available: Experimental details of the syntheses, CIF files for both structural analyses and details of the molecular orbital calculations for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11. (b) Coupé J. N.; Jordão E.; Fraga M. A.; Mendes M. J. *Appl. Catal. A* **2000**, *199*, 45.
(2) (a) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1211. (b) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1211. (c) Hermans, S.; Johnson, B. F. G. *Chem. Commun.* **2000**, 1955.
(3) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *Inorg. Chem.* **2002**, *41*, 5593.
(4) (a) Preut, H.; Haupt, H.-J.; Florke, U. *Acta Crystallogr., Sect. C* **1984**, *40*, 600. (b) Haupt, H.-J.; Balsaa, P.; Schwab, B.; Florke, U.; Preut, H. *Z. Anorg. Allg. Chem.* **1984**, *22*, 513. (c) Narayanan, B. A.; Kochi, J. K. *Inorg. Chim. Acta* **1986**, *122*, 85. (d) Westerberg, D. E.; Sutherland, B. E.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 1642. (e) Huie, B. T.; Kirtley, S. W.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1981**, *213*, 45.
(5) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644.
(6) 200.0 mg of Ph$_3$SnH (0.57 mmol) and 75 mg of Re$_2$(CO)$_8$(μ-CH═CHBn)(μ-H) (0.11 mmol) in 35 mL of hexane was heated to reflux for 2 h. The product was separated by TLC using a 3:1 hexane/methylene chloride solvent mixture to yield 64.8 mg (52%) of yellow Re$_2$(CO)$_8$(μ-SnPh$_2$)$_2$. Spectral data: IR ν_{CO} (cm^{-1} in hexane): 2060 (m), 2008 (s), 1981 (m), 1972 (m); ^{1}H NMR (CD$_2$Cl$_2$ in ppm): $\delta = 7.69$ (m, 8 H, Ph), 7.46 (m, 8 H, Ph), 7.41 (m, 4 H, Ph).
(7) Crystal data for **1**: Re$_2$Sn$_2$O$_8$C$_{32}$H$_{20}$, $M_r = 1142.26$, triclinic, space group $P1$, $a = 9.5962(5)$ Å, $b = 12.6495(7)$ Å, $c = 14.5038(8)$ Å, $\alpha = 104.342(1)°$, $\beta = 90.559(1)°$, $\gamma = 105.380(1)°$, $V = 1639.25(15)$ Å$_3$, $Z = 2$, $T = 296$ °C, Mo Kα = 0.71073 Å. The final $R_1(F^2)$ was 0.0372 for 6488 reflections $I > 2\sigma(I)$.
(8) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.
(9) (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. (b) Manson, J.; Webster, C. E.; Hall, M. B. *JIMP*, Development Version 0.1 (built for Windows PC and Redhat Linux 7.3), March 2003; Department of Chemistry, Texas A&M University, College Station, TX 77842 (http://www.chem.tamu.edu/jimp/). (c) *MOPLOT2*, for orbital and density plots from linear combinations of Slater or Gaussian type orbitals; version 2.0, June 1993; Dennis L. Lichtenberger, Department of Chemistry, University of Arizona, Tucson, AZ 85721. Complex **1** was modeled by the assembly of a Re$_2$(CO)$_8$ fragment and two SnH$_2$ fragments using idealized D_{2h} symmetry.
(10) 56.0 mg of Pd(PBu$^t_3$)$_2$ (0.11 mmol) was added to a solution of 25 mg of **1** (0.022 mmol) in 25 mL of CH$_2$Cl$_2$. The solution was stirred at 25 °C for 30 min. The product was isolated by TLC (silica gel) using a 2:1 hexane/methylene chloride solvent to yield 24.9 mg (67%) of orange Re$_2$(CO)$_8$(μ-SnPh$_2$)$_2$[Pd(PBu$^t_3$)]$_2$, **2**. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2074 (w), 2047 (w), 2035 (w), 1998 (s), 1994 (m), 1980 (s), 1962 (m), 1955 (vs), 1821 (w); ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 7.79$ (m, 8 H, Ph), 7.32 (m, 8 H, Ph), 7.27 (m, 4 H, Ph), 1.24 (d, 54 H, CH$_3$, $^3J_{P-H} = 13$ Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = 85.4$ (s, 2 P).
(11) Crystal data for **2**: Pd$_2$Re$_2$Sn$_2$P$_2$O$_8$C$_{56}$H$_{74}$, $M_r = 1759.67$, triclinic, space group $P\bar{1}$, $a = 10.8119(7)$ Å, $b = 12.4429(8)$ Å, $c = 12.9946(8)$ Å, $\alpha = 80.117(1)°$, $\beta = 68.988(1)°$, $\gamma = 71.927(1)°$, $V = 1547.82(17)$ Å^3, $Z = 2$, $T = 293$ °C, Mo Kα = 0.71073 Å. The final $R_1(F^2)$ was 0.0332 for 4901 reflections $I > 2\sigma(I)$.
(12) Trebbe, R.; Schager, F.; Goddard, R.; Pörschke, K.-R. *Organometallics* **2000**, *19*, 521.
(13) (a) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *J. Am. Chem.* Soc. **2002**, *124*, 5628. (b) Adams, R. D.; Captain, B.; Fu, W.; Pellechia, P. J.; Smith, M. D. *Inorg. Chem.*, **2003**, *42*, 2094. (c) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *J. Organomet. Chem.* **2003**, *682*, 113. (d) Adams, R. D.; Captain, B.; Zhu, L. *J. Am. Chem. Soc.* **2004**, *126*, 3042. (e) Adams, R. D.; Captain, B.; Fu, W.; Smith, J. L. Jr.; Smith, M. D. *Organometallics* **2004**, *23*, 589. (f) Adams, R. D.; Captain, B.; Pellechia, P. J.; Smith, J. L., Jr. *Inorg. Chem.*, **2004**, *43*, 2695. (g) Adams, R. D.; Captain, B.; Fu, W.; Hall, M. B.; Manson, J.; Smith, M. D.; Webster, C. E. *J. Am. Chem.* Soc. **2004**, *126*, 5253. (h) Adams, R. D.; Captain, B.; Smith, M. D. *J. Cluster Sci.* **2004**, *15*, 139. (i) Adams, R. D.; Captain, B.; Fu, W.; Hall, M. B.; Smith, M. D.; Webster, C. E. *Inorg. Chem.*. **2004**, *43*, 3921.
(14) (a) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. *Acc. Chem. Res.* **2003,** *36*, 20. (b) Thomas, J. M.; Raja, R.; Johnson, B. F. G.; Hermans, S.; Jones, M. D.; Khimyak, T. *Ind. Eng. Chem. Res.* **2003**, *42*, 1563. (c) Johnson B. F. G. *Top. Catal.* **2003**, *24*, 147. (d) Moreno-Manas, M.; Pleixats, R. *Acc. Chem Res.* **2003**, *36*, 638.

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